Theory of Ferroelectric Nanoparticles in Nematic Liquid Crystals

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Recent experiments have reported that ferroelectric nanoparticles have drastic effects on nematic liquid crystals—increasing the isotropic-nematic transition temperature by about 5 K, and greatly increasing the sensitivity to applied electric fields. To understand these effects, we develop a theory for the statistical mechanics of ferroelectric nanoparticles in liquid crystals. This theory predicts the enhancements of liquid-crystal properties, in good agreement with experiments. These predictions apply even when electrostatic interactions are partially screened by moderate concentrations of ions.

In recent years, many experiments have found that colloidal particles in nematic liquid crystals exhibit remarkable new types of physical phenomena. If the particles are micron-scale, they induce an elastic distortion of the liquid-crystal director. This elastic distortion leads to an effective interaction between particles, and offers the possibility of organizing a periodic array of particles, with possible photonic applications [1, 2, 3, 4, 5, 6]. If the particles are 10–100 nm in diameter, they are too small to distort the liquid-crystal director, and hence the system enters another range of behavior. Experiments have shown that low concentrations of *ferroelectric* nanoparticles can greatly enhance the physical properties of nematic liquid crystals [7, 8, 9, 10, 11, 12, 13, 14]. In particular, $Sn_2P_2S_6$ or $BaTiO_3$ nanoparticles at low concentration (<1%) increase the orientational order parameter of the host liquid crystal, and increase the isotropic-nematic transition temperature by about 5 K. The nanoparticles also decrease the switching voltage for the Fredericksz transition. These experimental results are important for fundamental nanoscience, because they show that nanoparticles can couple to the orientational order of a macroscopic medium. They are also important for technological applications, because they provide a new opportunity to tune the properties of liquid crystals without additional chemical synthesis.

A key question in this field is how to understand and control the properties of liquid crystals doped with ferroelectric nanoparticles. One paper has argued that the nanoparticles produce large local electric fields, which polarize the liquid-crystal molecules and thereby increase the intermolecular interaction [13]. This increased interaction leads to a higher isotropic-nematic transition temperature T_{NI}. A limitation of this approach is that it does not consider the orientational distribution of the nanoparticles themselves. One might expect this distribution to be crucial for understanding how nanoparticles affect the orientational order of the liquid crystal.

In this paper, we propose a new theory for the statistical mechanics of ferroelectric nanoparticles in liquid crystals, which is based specifically on the orientational distribution of the nanoparticle dipole moments. This distribution is characterized by an orientational order parameter, which interacts with the orientational order of the liquid crystals and stabilizes the nematic phase. We estimate the coupling strength and calculate the resulting enhancement in T_{NI}, in good agreement with experiments. This enhancement occurs even when electrostatic interactions are partially screened by moderate concentrations of ions in the liquid crystal. In addition, we predict the response of the isotropic phase to an applied electric field, known as the Kerr effect, and show that it is greatly enhanced by the presence of nanoparticles.

To begin the calculation, consider a spherical nanoparticle with radius R and electrostatic dipole moment $\mathbf{p}$, surrounded by a nematic liquid crystal, as shown in Fig. 1. The electric field $\mathbf{E}$ generated by the nanoparticle interacts with the order tensor $Q_{\alpha\beta}^{LC}$ of the liquid crystal through the free energy

$$F_{int} = -\frac{\epsilon_0 \Delta\epsilon}{3} \int d^3r\, Q_{\alpha\beta}^{LC}(\mathbf{r}) E_\alpha(\mathbf{r}) E_\beta(\mathbf{r}), \qquad (1)$$

where $\Delta\epsilon$ is the dielectric anisotropy of the fully aligned liquid crystal. The electric field of the nanoparticle has the standard dipolar form

$$\mathbf{E}(\mathbf{r}) = \frac{1}{4\pi\epsilon_0\epsilon} \left(\frac{3\mathbf{r}(\mathbf{r}\cdot\mathbf{p})}{r^5} - \frac{\mathbf{p}}{r^3} \right), \qquad (2)$$

neglecting higher-order corrections due to the dielectric anisotropy of the liquid crystal. Near the nanoparticle,
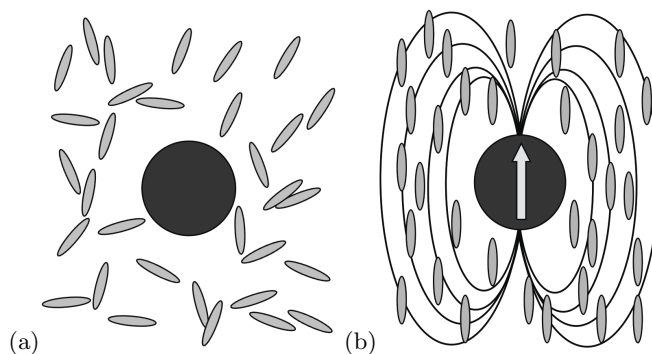

FIG. 1: Nanoparticles surrounded by liquid crystal. (a) Particle with no electric dipole moment, in the isotropic phase. (b) Ferroelectric particle with electric dipole moment, which produces an electric field that interacts with the orientational order of the liquid crystal.

the electric field varies rapidly as a function of position. However, the liquid-crystal order cannot follow that rapid variation, because it would cost too much elastic energy. Hence, for sufficiently small nanoparticles, we can assume that order tensor $Q_{\alpha\beta}^{\mathrm{LC}}$ is uniform in space. In that case, we can integrate the interaction free energy to obtain

$$F_{\mathrm{int}} = -\frac{\Delta\epsilon}{180\pi\epsilon_0\epsilon^2 R^3} Q_{\alpha\beta}^{\mathrm{LC}} p_\alpha p_\beta. \tag{3}$$

Now consider a low concentration ρ_{NP} of nanoparticles dispersed in the liquid crystal. The dipole moments of these nanoparticles will not all have the same orientation; rather there must be a distribution of orientations. As a result, the interaction of liquid crystal and nanoparticles gives the free energy density per unit volume

$$\frac{F_{\mathrm{int}}}{V} = -\frac{\Delta\epsilon\rho_{\mathrm{NP}}}{180\pi\epsilon_0\epsilon^2 R^3} Q_{\alpha\beta}^{\mathrm{LC}} \langle p_\alpha p_\beta\rangle, \tag{4}$$

averaged over the distribution of nanoparticle orientations. This distribution can be expressed in terms of a nanoparticle order tensor

$$Q_{\alpha\beta}^{\mathrm{NP}} = \frac{3}{2}\frac{\langle p_\alpha p_\beta\rangle}{p^2} - \frac{1}{2}\delta_{\alpha\beta}, \tag{5}$$

analogous to the standard liquid-crystal order tensor. Hence, the interaction free energy density becomes

$$\frac{F_{\mathrm{int}}}{V} = -\frac{\Delta\epsilon\rho_{\mathrm{NP}}p^2}{270\pi\epsilon_0\epsilon^2 R^3} Q_{\alpha\beta}^{\mathrm{LC}} Q_{\alpha\beta}^{\mathrm{NP}}, \tag{6}$$

which shows an explicit coupling between the order tensor of the liquid crystal and the order tensor of the nanoparticles. If we make the reasonable assumption that both of these tensors are aligned along the same axis, then this interaction reduces to

$$\frac{F_{\mathrm{int}}}{V} = -\frac{\Delta\epsilon\rho_{\mathrm{NP}}p^2}{180\pi\epsilon_0\epsilon^2 R^3} S_{\mathrm{LC}} S_{\mathrm{NP}}, \tag{7}$$

where S_{LC} and S_{NP} are the scalar order parameters of the liquid crystal and the nanoparticles, respectively.

To model the statistical mechanics of nanoparticles dispersed in the liquid crystal, we must expand the free energy in *both* order parameters S_{LC} and S_{NP}, which gives

$$\begin{aligned}\frac{F}{V} &= \frac{a_{\mathrm{LC}}'(T-T^*)}{2}S_{\mathrm{LC}}^2 - \frac{b}{3}S_{\mathrm{LC}}^3 + \frac{c}{4}S_{\mathrm{LC}}^4 \\ &\quad + \frac{a_{\mathrm{NP}}}{2}S_{\mathrm{NP}}^2 - \frac{\Delta\epsilon\rho_{\mathrm{NP}}p^2}{180\pi\epsilon_0\epsilon^2 R^3}S_{\mathrm{LC}}S_{\mathrm{NP}}.\end{aligned} \tag{8}$$

Here, the first three terms are the standard Landau-de Gennes free energy of a nematic liquid crystal. The first-order isotropic-nematic transition of the pure liquid crystal occurs at $T_{\mathrm{NI}} = T^* + (2b^2)/(9a_{\mathrm{LC}}'c)$, and the leading coefficient in this expansion can be estimated through Maier-Saupe theory as $a_{\mathrm{LC}}' = 5k_{\mathrm{B}}\rho_{\mathrm{LC}}$, where ρ_{LC} is the concentration of liquid-crystal molecules per volume [15].

The fourth term in the free energy is the entropic cost of imposing orientational order on the nanoparticles. By expanding the entropy in terms of the orientational distribution function of the nanoparticles, we can estimate the coefficient as $a_{\mathrm{NP}} = 5k_{\mathrm{B}}T\rho_{\mathrm{NP}}$. The final term is the coupling between the liquid-crystal order and the nanoparticle order, calculated above.

We minimize the free energy of Eq. (8) over the nanoparticle order parameter to find the optimum value

$$S_{\mathrm{NP}} = \frac{\Delta\epsilon p^2}{900\pi\epsilon_0\epsilon^2 R^3 k_{\mathrm{B}}T} S_{\mathrm{LC}}. \tag{9}$$

This equation shows that the liquid crystal induces orientational order of the nanoparticles, with a nanoparticle order parameter proportional to the liquid-crystal order parameter. Note that the induced order is independent of the nanoparticle concentration, which is reasonable because it arises from interaction of individual nanoparticles with the liquid crystal, not from interactions between nanoparticles. We then substitute this expression back into the free energy to obtain

$$\begin{aligned}\frac{F}{V} &= \frac{a_{\mathrm{LC}}'}{2}\left[T - T^* - \frac{\rho_{\mathrm{NP}}^2}{a_{\mathrm{LC}}'a_{\mathrm{NP}}}\left(\frac{\Delta\epsilon p^2}{180\pi\epsilon_0\epsilon^2 R^3}\right)^2\right]S_{\mathrm{LC}}^2 \\ &\quad - \frac{b}{3}S_{\mathrm{LC}}^3 + \frac{c}{4}S_{\mathrm{LC}}^4.\end{aligned} \tag{10}$$

In this equation, the coefficient of S_{LC}^2 has been shifted by the interaction with the nanoparticles. This shift increases the isotropic-nematic transition temperature by

$$\begin{aligned}\Delta T_{\mathrm{NI}} &= \frac{\rho_{\mathrm{NP}}^2}{a_{\mathrm{LC}}'a_{\mathrm{NP}}}\left(\frac{\Delta\epsilon p^2}{180\pi\epsilon_0\epsilon^2 R^3}\right)^2 \\ &= \frac{\pi\phi_{\mathrm{NP}}R^3}{3T_{\mathrm{NI}}\rho_{\mathrm{LC}}}\left(\frac{2\Delta\epsilon P^2}{675k_{\mathrm{B}}\epsilon_0\epsilon^2}\right)^2.\end{aligned} \tag{11}$$

The last expression has been simplified by writing $p = (\frac{4}{3}\pi R^3)P$ and $\rho_{\mathrm{NP}} = \phi_{\mathrm{NP}}/(\frac{4}{3}\pi R^3)$, where P is the polarization and ϕ_{NP} the volume fraction of the nanoparticles.

To estimate ΔT_{NI} numerically, we use the following parameters appropriate for $Sn_2P_2S_6$ nanoparticles in the liquid crystal 5CB: $\phi_{\mathrm{NP}} = 0.5\%$, $R = 35$ nm, $T_{\mathrm{NI}} = 308$ K, $\rho_{\mathrm{LC}} = 2.4 \times 10^{27}$ m^{-3}, $P = 0.04$ Cm^{-2}, $k_{\mathrm{B}} = 1.38 \times 10^{-23}$ JK^{-1}, $\epsilon_0 = 8.85 \times 10^{-12}$ C^{2}N^{-1}m^{-2}, and $\Delta\epsilon \approx \epsilon \approx 10$ [16]. With those parameters, we obtain $\Delta T_{\mathrm{NI}} \approx 5$ K, which is roughly consistent with the increase that is observed experimentally. Of course, there is a substantial uncertainty in this estimate, because the parameters R and P are not known very precisely in the experiments.

Note that our model predicts that the enhancement ΔT_{NI} should be first-order in volume fraction ϕ_{NP}, fourth-order in polarization P, and third-order in R. In particular, increasing R should increase ΔT_{NI} as long as the nanoparticles are not large enough to disrupt the liquid-crystal order. This prediction disagrees with

Ref. [13], which predicts that ΔT_{NI} should be first-order in ϕ_{NP}, second-order in P, and independent of R.

At this point, we must consider the effects of ionic impurities in the liquid crystal. Any liquid crystal contains some concentration of free positive and negative ions, which can redistribute in response to electric fields. One might worry that these ions would screen the electric field of the nanoparticles, and hence prevent the enhancement of T_{NI}. To address this issue, we solve the linearized Poisson-Boltzmann equation to find the electric field around a dipole in the presence of ions

$$\mathbf{E}(\mathbf{r}) = \frac{e^{-\kappa r}}{4\pi\epsilon_0\epsilon} \left[(1+\kappa r)\left(\frac{3\mathbf{r}(\mathbf{r}\cdot\mathbf{p})}{r^5} - \frac{\mathbf{p}}{r^3} \right) + \frac{\kappa^2\mathbf{r}(\mathbf{r}\cdot\mathbf{p})}{r^3} \right]. \tag{12}$$

In this expression, κ^{-1} is the Debye screening length given by

$$\kappa^{-1} = \left(\frac{\epsilon_0\epsilon k_{\text{B}}T}{2nq^2} \right)^{1/2}, \tag{13}$$

where n is the concentration and q the charge of the ions. With this expression for the field, we can repeat the calculation above for the enhancement in T_{NI}, leading to

$$\Delta T_{\text{NI}} = \frac{\pi\phi_{\text{NP}}R^3}{3T_{\text{NI}}\rho_{\text{LC}}} \left(\frac{2\Delta\epsilon P^2}{675 k_{\text{B}}\epsilon_0\epsilon^2} \right)^2 e^{-2\kappa R}$$
$$\times \left(1 + 2\kappa R + \kappa^2 R^2 + \kappa^3 R^3 \right). \tag{14}$$

To interpret this result, note that the key parameter is κR, the ratio of the nanoparticle radius to the Debye screening length. If the ion concentration is low, then the screening length is large compared with the nanoparticle radius, and hence ΔT_{NI} is as large as in the unscreened case. However, if the ion concentration is sufficiently high, then the screening length becomes comparable to the nanoparticle radius, and hence the enhancement is screened away. For a specific example, Fig. 2 shows T_{NI} as a function of ion concentration n, using the numerical parameters discussed above. In this example, the full unscreened enhancement persists up to $n \approx 10^{20}$ ions/m^3. It then decays away as a function of ion concentration, and is virtually eliminated by $n \approx 10^{23}$ ions/m^3.

Typical measurements of the ion concentration in 5CB show $n \approx 10^{20}$ ions/m^3 and hence $\kappa^{-1} \approx 260$ nm [17]. Because this screening length is much greater than the nanoparticle radius, the enhancement should indeed be observable in realistic experiments. Note that the ion concentration in a liquid crystal varies over several orders of magnitude, depending on preparation conditions. Hence, we speculate that variations in ion concentration may be one explanation for variations in published experimental measurements of ΔT_{NI}.

So far, we have modeled the spontaneous ordering of a nanoparticle-doped liquid crystal. We can also use the same theoretical approach to predict how the system responds to an applied electric field. For a specific example,
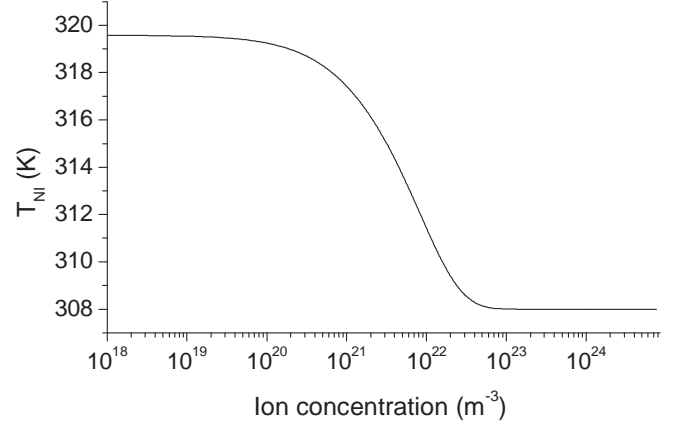

FIG. 2: Predicted isotropic-nematic transition temperature as a function of ion concentration in a nanoparticle-doped liquid crystal, using numerical parameters presented after Eq. (11).

we investigate the Kerr effect, in which an applied electric field $\mathbf{E}$ induces orientational order in the isotropic phase, slightly above the isotropic-nematic transition. In a pure liquid crystal, the Kerr effect is a weak alignment proportional to E^2. In a liquid crystal doped with ferroelectric nanoparticles, we expect that an applied electric field will induce *polar* order of the nanoparticles, proportional to E. This polar order will necessarily induce *nematic* order of the nanoparticles, proportional to E^2, which will in turn induce nematic order of the liquid crystal, also proportional to E^2. Hence, the nanoparticle-doped liquid crystal should have an enhanced Kerr effect with the same symmetry as the standard Kerr effect, but with a much larger magnitude.

To model the enhanced Kerr effect, we must generalize the Landau theory presented above in three ways. First, we must introduce a polar order parameter $M_\alpha = \langle p_\alpha \rangle / p$ for the nanoparticles, as well as the nematic order parameters $Q_{\alpha\beta}^{\text{NP}}$ and $Q_{\alpha\beta}^{\text{LC}}$. Second, we must consider the energetic coupling of an applied electric field to the order parameters. In the free energy density, an applied field couples linearly to the polar order parameter of the nanoparticles through the interaction $-\rho_{\text{NP}}pE_\alpha M_\alpha$, and couples quadratically to the nematic order parameter of the liquid crystal through the interaction $-\frac{1}{3}\epsilon_0\Delta\epsilon E_\alpha E_\beta Q_{\alpha\beta}^{\text{LC}}$. Third, we must calculate the entropy of a nanoparticle distribution characterized by both order parameters M_α and $Q_{\alpha\beta}^{\text{NP}}$, following the method of Ref. [15]. Assuming that all order parameters are aligned along the electric field direction, the free energy becomes

$$\frac{F}{V} = \frac{a'_{\text{LC}}(T-T^*)}{2}S_{\text{LC}}^2 - \frac{b}{3}S_{\text{LC}}^3 + \frac{c}{4}S_{\text{LC}}^4 - \frac{\epsilon_0\Delta\epsilon}{3}E^2 S_{\text{LC}}$$
$$- \frac{\Delta\epsilon\rho_{\text{NP}}p^2}{180\pi\epsilon_0\epsilon^2 R^3}S_{\text{LC}}S_{\text{NP}} - \rho_{\text{NP}}pEM \tag{15}$$
$$+ k_{\text{B}}T\rho_{\text{NP}} \left(\frac{5}{2}S_{\text{NP}}^2 + \frac{3}{2}M^2 - 3S_{\text{NP}}M^2 \right).$$
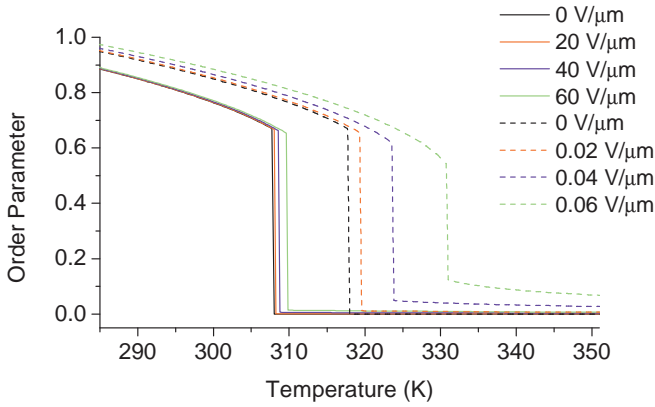
FIG. 3: (Color online) Prediction for field-induced order parameter $S_{\rm LC}$ as a function of temperature for several values of applied electric field, with and without ferroelectric nanoparticles, using numerical parameters presented after Eq. (11).

We minimize this free energy over all three order parameters, M, $S_{\rm NP}$, and $S_{\rm LC}$. In the high-temperature isotropic phase, in the limit of small electric field, the resulting liquid-crystal order parameter is

$$S_{\rm LC} = \frac{\epsilon_0 \Delta\epsilon E^2}{3a'_{\rm LC}(T - T^* - \Delta T_{\rm NI})} \left[1 + \frac{\phi_{\rm NP}}{3} \left(\frac{4\pi P^2 R^3}{45\epsilon_0 \epsilon k_{\rm B} T} \right)^2 \right].$$

(16)

In this expression, note that the induced order parameter depends on electric field and temperature exactly as in the standard Kerr effect, but the coefficient is increased by the coupling with nanoparticles. In the square brackets, the first term of 1 indicates the standard Kerr effect for pure liquid crystals, and the second term indicates the relative enhancement due to nanoparticle doping.

For a specific numerical example, we use the same parameters presented after Eq. (11). With these parameters, the relative enhancement in the Kerr effect is extremely large, of order 10^7. Figure 3 plots the predicted order parameter $S_{\rm LC}$ as a function of temperature for several values of the applied electric field, with and without nanoparticles. This plot shows explicitly that the presence of nanoparticles greatly enhances the sensitivity to applied electric fields in the isotropic phase, as well as enhancing the isotropic-nematic transition temperature. This prediction should be tested in future experiments, and should provide an opportunity to build liquid-crystal devices that can operate at lower electric fields.

As a final point, we should mention one limitation of our model. Like all Landau theories, our model involves an expansion of the free energy in powers of the order parameters, and hence it overestimates the order parameters that occur in the low-temperature phase. Future work may extend this model through asymptotic low-temperature approximations to the free energy. Nevertheless, our current model clearly shows that effects of nanoparticle doping at and above the isotropic-nematic transition, in the regime where Landau theory is valid.

In conclusion, we have developed a theory for the statistical mechanics of ferroelectric nanoparticles in nematic liquid crystals. This theory predicts the enhancement in the isotropic-nematic transition temperature and in the response to an applied electric field, which can be tested experimentally. The work demonstrates the coupling of nanoparticles with macroscopic orientational order, and provides an opportunity to improve the properties of liquid crystals without chemical synthesis.

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